SELF-ASSOCIATION, STRUCTURE, INTERACTION, AND DYNAMICS OF RATAWI ASPHALTENES IN SOLVENTS

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INTRODUCTION

Asphaltene is a class of petroleum material commonly recognized as the heptane insoluble, but toluene soluble fraction of either the crude oil or the vacuum residue [1]. Asphaltene has long been suspected as the key component hindering refining yields, through micellization [2]. Although this scenario has been speculated, direct evidence was not available until recently [3,4]. Of particular importance is the direct evidence for asphaltene micellization, which correlates asphaltene properties with surfactants.

In this paper, we systematically report findings from our asphaltene study, in organic solvents. First, we measured the surface tension as a function of asphaltene concentration in pyridine to identify the critical micelle concentration. This experiment provided direct evidence of asphaltene self-association. Secondly, we characterized the rheological behavior of the asphaltene micellar solutions, from which hydrodynamic properties were quantified. Thirdly, the structure of the micelles were measured using small angle neutron scattering, along with the interactions between the micelles. Finally, we measured the dielectric relaxation of the asphaltene solutions in toluene, in order to investigate the forces that initiate micellization.

EXPERIMENTAL

Samples

Asphaltenes were derived from Ratawi (Neutral Zone) Vacuum Residue by solvent fractionation. One gram of vacuum residue (VR) was mixed with 40 cm^3 of heptane (HPLC grade), and stirred overnight. Heptane insolubles (C7I or asphaltenes) were extracted using Whatman number 5 filter paper and dried under a stream of nitrogen. Mass balances were performed to ensure complete solvent removal. The asphaltenes were redissolved in appropriate solvents, disscussed below, prior to measurements.

Surface Tension Measurements

Surface tension was measured as a function of asphaltene concentration in pyridine (from 0% to 1% by weight) with a Krüss K10ST Surface Tensiometer, using the Wilhelmy plate method. The details of this instrument and the technique used have been given elsewhere [5].

Zero-Shear Viscosity

Viscosity measurements were performed for asphaltene fractions in toluene as a function of concentration for volume fractions from 0.01 and 0.30, at room temperature, on a Brookfield Viscometer. The instrument's working range was from 0-1000 X 10^{-3} Pa-s and a 0.1% accuracy of full scale.

Small Angle Neutron Scattering

The small angle neutron scattering (SANS) measurements were conducted on the time-of-flight small angle diffractometer (SAD) at Argonne National Laboratory. The scattering vector covered a range from 0.007 to 0.34 $Å^{-1}$. In this experiment we measured asphaltenes in a series of deuterated toluene/pyridine mixtures for several asphaltene concentrations to study both the structure and polydispersity dependences on concentration and on solvent permittivity. All the measurements were performed at 22 ^{o}C.

Dielectric Relaxation Measurements

Dielectric relaxations were measured for asphaltene solutions, using an HP 4192A low frequency (5 Hz to 13 MHz) impedance analyzer. The cell used was an immersion type cell from Rosemont Analytical, consisting of four platinum black coated electrodes, with 1mm interplate spacing and a total area of 9 cm^2. The HP 4192A impedance analyzer measures the capacitance between the plates from which the dielectric storage ϵ' and the dielectric loss ϵ'' ($= \epsilon'/D$, D is the measured quality factor) can be computed according to $\epsilon' = C \cdot d/\epsilon_0 A$, where C is the capacitance, d is the electrode spacing, ϵ_0 is the calibration constant ($= 8.8854$ X 10^{-12} F/m), and A is the total electrode area.

RESULTS AND DISSCUSSION

Surface Tension

Fig. 1 shows the surface tension as a function of asphaltene concentration in pyridine. A breaking point was observed at ~ 0.025 wt%, signifying that there is an onset of self-association of asphaltenic molecules at this concentration. This phenomenon is similar to the micellization of surfactant molecules in aqueous solutions. In a previous report we had shown that the self-association of asphaltene molecules in organic solvents was reversible, and more or less followed the micellar thermodynamics [3].

Zero-Shear Viscosity

Fig. 2a shows a typical zero-shear relative viscosity plot for asphaltene in toluene, as a function of asphaltene volume fraction. As expected, the relative viscosity follows the Einstein's argument (linear) in the dilute regime, and gradually deviates from it as concentration increases. This is due to the combination effect of solvation, interparticle interaction, as well as the particle shape. Fig. 2b exhibits the analysis suggested by Pal and Rhodes [6]. In their argument, the zero-shear viscosity should exhibit linearity if the viscosity is plotted as $(1/\eta_r)^{0.4}$ versus Φ, where η_r is

the relative viscosity and Φ the volume fraction of asphaltene. The slope of the curve, k, is the solvation constant, representing the effect of solvation, provided the shape effect is negligible. The k value obtained from Fig. 2b was 2.79, different from unity which represents no solvation. Fig. 2c compares the viscosity behavior of asphaltene colloids with a hard sphere model, taking the solvation effect into account. The viscosity for the hard sphere model was developed based on the hopping probability of the particle in a percolated environment [7]. Based on this argument, Campbell and Forgacs derived a simple equation for a hard sphere system with a volume fraction higher than the percolation threshold, which is in the neighborhood of 0.16 for most colloidal systems [8]. As one can see from Fig. 2c, for volume fractions up to about 0.3, there is no appreciable difference. This explains why the shape effect can be neglected in Pal and Rhodes analysis (it still shows linearity, although Pal and Rhodes's argument is only applicable for hard sphere systems). The effect of interparticle interaction was analyzed using an equation derived by Grimson and Barker [10]. They derived the zero-shear viscosity for a $(1/r^n)$ potential. The equation reads

$$\eta = (1+2.5\Phi) + \eta_o(\Phi/\Phi_m)[1-(\Phi/\Phi_m)^{1/3}]^{-n}$$

where Φ_m is the maximum packing volume fraction (it was estimated to be about 0.64 for asphaltene in toluene [9]). With this equation we found that the interactions between asphaltene colloids can be well described by $1/r^2$ potential (see Fig. 2d).

As a summary from our zero-shear viscosity analysis, we found the asphaltene colloids in toluene to be solvated, but behaved rheologically like hard spheres for Φ up to ~ 0.3, and the interparticle interactions followed a $1/r^2$ potential. In the following, we shall discuss the detailed structure, the polydispersity, and the interparticle interactions obtained from a small angle neutron scattering study.

Small Angle Neutron Scattering

Small angle neutron scattering (SANS) measures the differential cross section per unit volume of the sample, based on the scattering of the nuclei contained in the sample. In our case, the scatterers are the solvent (toluene/pyridine) and the asphaltene. Since asphaltene molecules contain nuclei different from toluene/pyridine, the capability in scattering the defined incoming neutrons differs. This scattering contrast allows us to differentiate the suspended asphaltene colloids from the solvent material, in terms of their shapes and the interactions between them. The SANS measurement is usually represented in terms of the scattering intensity I(Q) as a function of the scattering vector Q (= $(4\pi/\lambda)\sin\theta$, λ is the neutron wavelength and θ the scattering angle). For colloidal system the I(Q) can often be expressed as [10]

$$I(Q) = N_p \cdot <P(Q)> \cdot <S(Q)>$$

where N_p is the number density of the asphaltene colloids, $<P(Q)>$ is the average form factor, containing the shape information and the size polydispersity as well. $<S(Q)>$ is the average structure factor describing the interactions between particles.

Fig. 3a shows I(Q), together with the theoretical curve, assuming the asphaltene to be spheres with a size distribution following the Schultz distribution function, and an $(1/r)\exp[-(\sigma r)]$ interparticle potential (σ is a constant characterizing the range of the interaction). Apparently, the agreement is reasonable. The SANS measurements were performed for a series of concentrations and solvents of various toluene to pyridine volume ratios, to study the effect of solvent permittivity (ϵ) . Fig. 3b and Fig. 3c show the effect of solvent permittivity on the particle radius (R), interaction range (i.e., σ) and on the particle polydispersity respectively. The particle radius was not sensitive to ϵ. However, σ decreased with increasing ϵ, which means that the interaction range becomes longer ranged upon increasing ϵ. This suggests that the asphaltene colloids are charged, and the interactions are mainly electrostatic. As ϵ increases, the charge dissociation is enhanced, and results in an increase in the charge screening length (or decrease in σ). As for polydispersity (Fig. 3c), the increasing polydispersity, with increasing ϵ, indicating that the solvent quality decreases as a function of ϵ [11].

Dielectric Relaxation

Fig. 4 gives the dielectric loss ϵ'' as a function of the frequency for a 20% asphaltene solution in toluene at 60 $^{\circ}$C (circles), together with a fitting curve (solid line). This fitting curve was based on the Cole-Cole equation,

$$\epsilon''(\omega) = \epsilon_{\infty} + \Delta\epsilon/[1 + (i\omega\tau)^{1-\beta}]$$

where ω is the frequency in Hz, ϵ_{∞} is the dielectric constant at ∞ frequency, $\Delta\epsilon$ is the difference between ϵ_{∞} and the zero-frequency ϵ, τ is the mean dielectric relaxation time, and β is an exponent signifying the stretch of the relaxation, due to the interactions between particles. When $\beta = 0$, the system is a noninteracting ideal system (in this case, the relaxation is called a Dybye relaxation). The fitting quality is not perfect, mainly due to the high polydispersity of the particle size (and may be shape as well). For some cases at lower temperature, a shoulder was exhibited. This is likely due to the formation of a second mode, either resulting from percolation, or networking of the suspended particles. The β values obtained through the Cole-Cole fitting for all temperatures were very different from zero, meaning that there are significant interactions which may interfere the dielectric response. This clearly indicates that the interaction is dipole moment driven, and is electrostatic, confirming the result drawn from SANS measurements.

Conclusion

We have systematically studied the physical properties of asphaltene solutions, using various techniques. The properties we observed can be summarized as follows: (1) asphaltenes are similar to surface active agents, since there exists a threshold concentration (for a give organic solvent), above which the molecules self-associate into "micelles", (2) the aggregates are loosely packed (highly solvated), but with rheological behavior very similar to a hard sphere system until the volume fraction exceeds 0.3, (3) the interactions derived from the solution viscosity follows a $1/r^2$ potential, (4) the aggregates are charged and have significant size polydispersity, and (5) the interparticle interactions are electrostatic force driven.

References

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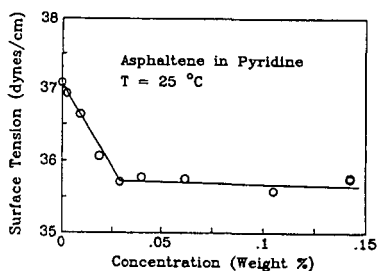
Fig. 1. Surface Tension of Asphal-
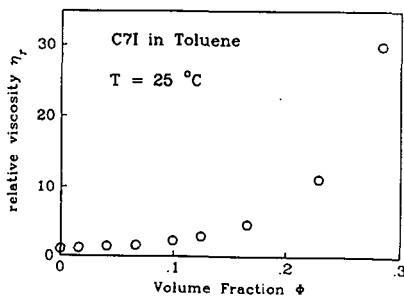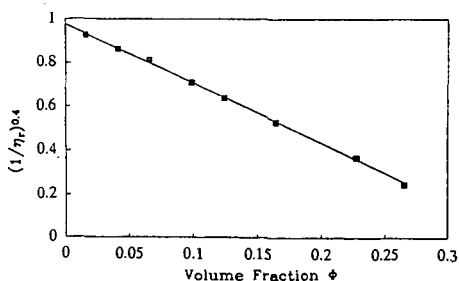tene as a function of concentration.

Fig. 2a. Relative viscosity
for asphaltene/toluene solution.

Fig. 2b. Pal and Rhodes Analysis.